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Five naphthalene azo benzene ligands complexed with copper metals: An excellent *in-situ* catecholase catalyst

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ABSTRACT

In order to mimic the function of catecholase activity, in situ copper (II) complexes of five ligands containing benzene and naphthalene moieties ponded by dazenyl groups: (E)-1-((2-methoxyphenyl)diazenyl)naphthalen-2-ol L1, (E)-1-((3-methoxyphenyl)diazenyl)naphthalen-2-ol L2, (E)-1- ((4-methoxyphenyl)diazenyl)naphthalen-2-ol L3, (E)-1-((2,4,6-tribromophenyl)diazenyl)naphthalen-2-ol L4, and (E)-1-((3-nitrophenyl)diazenyl)naphthalen-2-ol L5 were reported and examined, in combination with different copper salts, for their catecholase activities at ambient conditions. All complexes of tested ligands catalyze the studied reaction with the rate ranging from higher 25.1 μmol L^{-1} min^{-1} for the combination of two equivalents of ligand and one equivalent of metal in methanol, to weaker rate of 0.51 μmol L^{-1} min^{-1} for the combination of one equivalent of ligand and two equivalent of metal salt in methanol.

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1. Introduction

Development of enzyme biomimetic oxidation catalysts incorporating Cu(II) ion is great challenges for a chemists [1,2]. For examples, various heterocyclic ligands to reproduce catecholase activity [3–13]. These experiences aim to mimic the environment of the metal active site of this enzyme and also to better understand this function which is often assigned to metalloproteines containing copper like catechole oxidase [14], which is known to have two copper (II) ions similar to histidine nitrogen's ligands [15], this enzyme catalyses the oxidation of catechol to corresponding *o*-quinone through the four-electron reduction of molecular oxygen to water [16]. In attempt to mimic the active site function of catechol oxidase, many ligands models based on iron [17], copper [18], and cobalt [19] complexes have been designed and extensively studied [20–32]. In the continuation of looking for other ligands to be tested in such reaction comes this work which concerns azo compounds [33–35]. It has been known for many years that the azo compounds are a widely used class of dyes due to their application in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastics and electrochemical sensors [36]. Recently, 1-phenylazo-2-naphthol derivatives have attracted attention because the phenylazo-naphtholate group can provide N,O-bidentate chelation to stabilize transition or main group metal complexes [37]. Azo-metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their applications in molecular memory storage, non-linear optical elements and printing systems. Another advantage of complexes involving azo dyes and pigments and transition metal ions is the possibility to obtain new compounds with biological activity [38,39]. Herein, five ligands containing naphthalene and benzene moieties ponded by aza group are reported and studied for their catecholase activity. The results revealed that the trend of catecholase- like activity correlated to the sort of the ligands, the type of solvent, and the

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composition ratios of ligands and metal salts as well as the type of anion in the metal salt.

2. Experimental

2.1. Ligands description

The five ligands L1-L5 (see Fig. 1) were known and prepared by the method of Wang et al. [33–35] since 2003 for similar aromatic azo–compounds. Diazotization of the aromatic amine followed by a coupling reaction with 2-naphthol. The structures of all the products were unambiguously established on the basis of their spectral analysis (IR, ^{1}H NMR and MS mass spectral data) (see Fig. 2).

The proton NMR spectra of the phenylazo-naphtholate ligands revealed signals between 7 and 8 ppm corresponding to the naphthalene protons (Fig. 3).

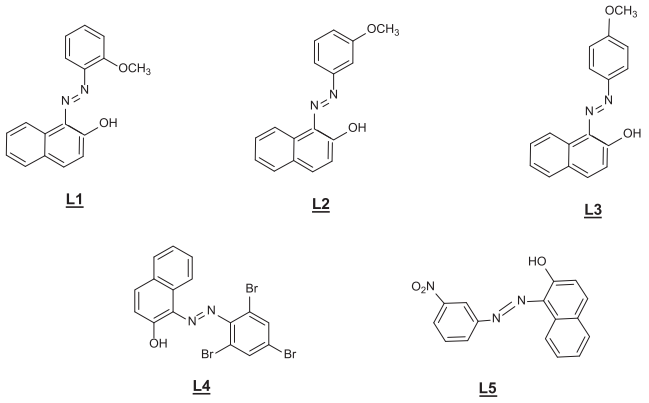

Fig. 1. Molecular structures of tested compounds L1-L5.

2.2. Catecholase-like activity measurements

The catecholase-like activities of the the complexes formed in situ by mixing successively 0.15 mL of a solution (2.10^{-3} mol/L) of copper salt CuX_2, nH_2O (with X = Cl^-, NO_3^-, CH_3COO^-, SO_4^{2-}) with 0.15 mL of ligand solution (2.10^{-3} mol/L) were performed for the oxidation of catechol (10^{-1} mol/L) with O_2 of air in methanol (99.99%) at ambient conditions. the evolution of product absorbance was followed at 390 nm according to time after regulation in zero on a spectrometer UV–Vis UV 1650 PC Shimadzo (FPN).

3. Result and discussion

3.1. Catalytic activity studies

- Reaction of catechol oxidation in the presence of copper complexes formed in situ with ligands L1–L5 in the Methanol solvent

Evaluation of the catecholase activity of these complexes was spectrophotometrically made by following the appearance of the maximum absorbance of the corresponding o-quinone at 390 nm over time (Fig. 4). The results for example are illustrated in Fig. 5 showing the change in absorbance at 390 nm versus time for 60 min. The obtained spectrum for catechol alone showed practically no absorbance as a function of time.

According to the obtained results in Table 1, it is clearly that all complexes formed in situ with the ligands L1-L5, catalyze the reaction of the oxidation of catechol to o-quinone, but with different rates which vary from 0.72 µmol L^{-1} min^{-1} for the complex formed by the pyrazole ligand L2 and the metal salt $CuCl_2$ as is weak catalyst to 19.54 µmol L^{-1} min^{-1} for the complex formed by the ligand L1 and the metal salt $Cu(NO_3)_2$ as is best catalyst.

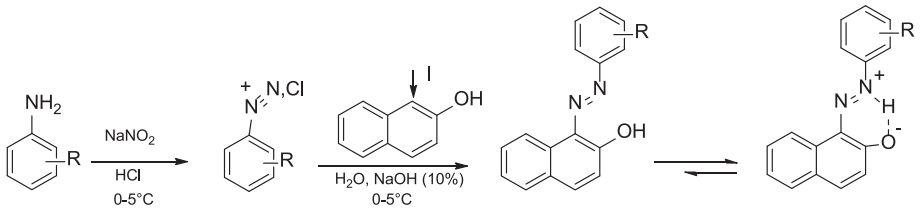

Fig. 2. Reaction route for compounds L1-L5.

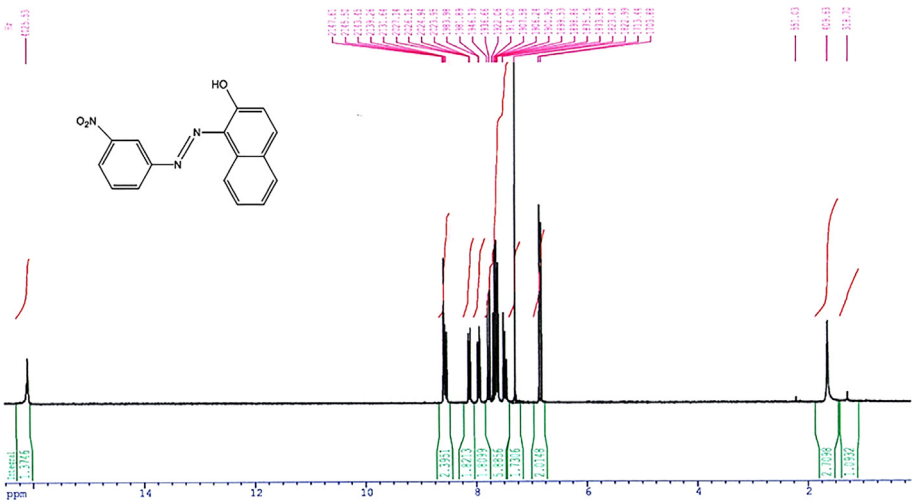

Fig. 3. Proton NMR spectrum for L5.

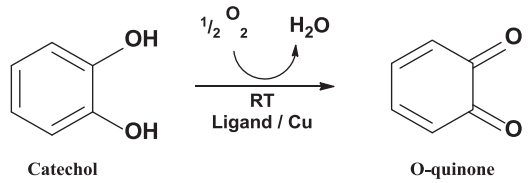

Fig. 4. Oxidation reaction of catechol.

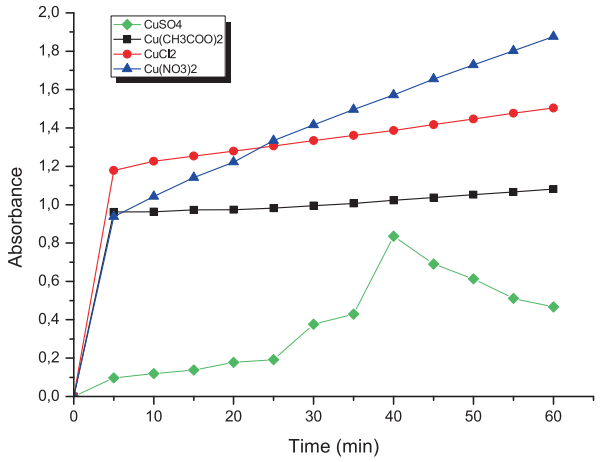

Fig. 5. Oxidation of catechol in the presence of complexes formed by L1 with various metal salts in methanol (Ligand/Salt: 1/1).

Table 1
Reaction rate V (μmol L^{-1} min^{-1}) of catechol oxidation in methanol (Ligand/Salt: 1/1).

	Reaction rate V (μmol L^{-1} min^{-1})			
Li/Salt	$CuSO_4$	$Cu(CH_3COO)_2$	$CuCl_2$	$Cu(NO_3)_2$
L1	4.86	11.26	15.66	19.54
L2	13.90	5.28	0.72	1.14
L3	2.47	12.69	2.08	1.11

Temperature: 25 °C; Solvent: Methanol; Absorbance maximal catechol: 390 nm; ε = 1600 L mol− 1 cm− 1.

We note that the oxidation rates depend strongly on booth the nature of the ligand and the type of anion. The rate of oxidation of catechol to o-quinone for the ligands studied is very high in the case ($L1/Cu(NO_3)_2$) combination in methanol and low in the case ($L2/CuCl_2$) complex in methanol. The change in reaction speed is related to the properties of the ligands, particularly the electronic effect of the substituent group which could have an effect on coordination.

The effect of the nature of the anion on the catalytic activity was noted, we note that the best results were obtained with the nitrate ions which allowed us to consider that the counter anion participates in the coordination environment and its nature influences well the catalytic activity of the complexes.

- Reaction of catechol oxidation in the presence of copper complexes formed in situ with ligands L1–L5 in the THF solvent

The nature of used solvent in reaction is an important factor for catecholased activity, the reaction rate of catechol oxidation will be influenced by solvent. In the last few years, a different work has shown that the nature of solvent has a large effect on the catecholase activity [40,41]. To more understand the effect of solvent on the catalysis of oxidation reaction of catechol, we carried out the same experiments under same condition, but by using the tetrahydrofuran (THF) as solvent, the absorbance of o-quinone are shown in Fig. 6.

As can be seen from Table 2 and Fig. 6, all complexes showed activity toward the oxidation of catechol. Different rates were

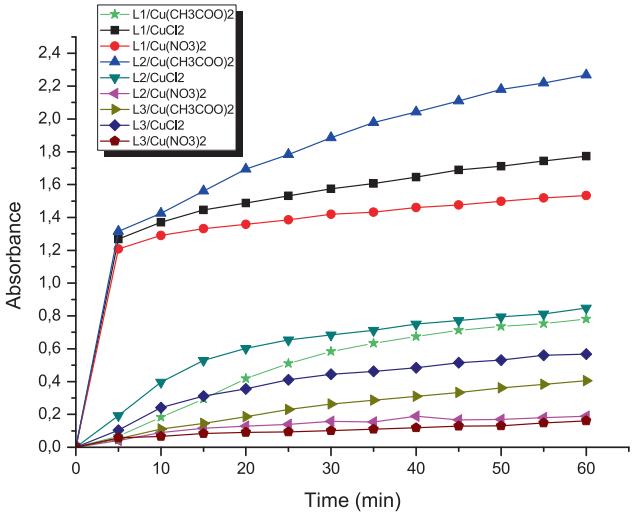

Fig. 6. Oxidation of Catechol in the presence of complexes formed by L1, L2, L3 with various metal salts in tetrahydrofuran (Ligand/Salt: 1/1).

Table 2
Reaction rate V (μmol L^{-1} min^{-1}) of catechol oxidation in tetrahydrofuran (Ligand/Salt: 1/1).

	Reaction rate V (μmol L^{-1} min^{-1})		
Li/Salt	$Cu(CH_3COO)_2$	$CuCl_2$	$Cu(NO_3)_2$
L1	8.13	18.46	15.97
L2	23.61	8.84	1.97
L3	4.22	5.91	1.7
L4	1.8	4.35	10.73
L5	4.73	6.53	13.03

Temperature: 25 °C; Solvent: THF; Absorbance maximal catechol: 390 nm; ε = 1900 L mol− 1 cm− 1.

Table 3
Reaction rate of catechol oxidation in methanol (Ligand/Salt: 1/2 and 2/1).

	$CuSO_4$		$Cu(CH_3COO)_2$		$CuCl_2$		$Cu(NO_3)_2$	
Li/Salt	2L/1M MeOH	1L/2M MeOH	2L/1M MeOH	1L/2M MeOH	2L/1M MeOH	1L/2M MeOH	2L/1M MeOH	1L/2M MeOH
L1	9.31	1.51	0.52	3.44	0.57	5.81	0.51	0.97
L2	3.12	2.35	6.78	11.54	23.44	1.48	4.13	1.25
L3	–	1.62	15.64	5.84	25.1	1.33	2.47	1.60

Temperature: 25 °C; Solvent: Methanol; Absorbance maximal catechol: 390 nm; ε = 1600 L mol− 1 cm− 1

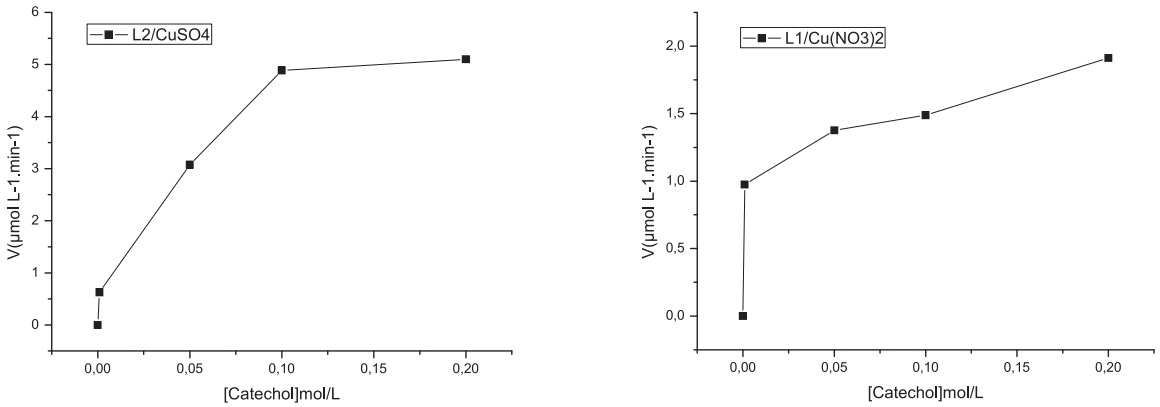

Fig. 7. The correlation between reaction rate and catechol concentrations catalyzed by various L1/Cu$(NO_3)_2$ and L2/$CuSO_4$ combinations.

obtained varying from 1.7 µmol L^{-1} min^{-1} for the complex formed by the ligand L3 and the metal salt Cu$(NO_3)_2$ as the weak catalyst to 23.61 µmol L^{-1} min^{-1} for the complex formed by L2/Cu$(CH_3COO)_2$ combination as the best catalyst . By comparing the reaction rates shown in Tables 1 and 2, we can reveal that the catecholase process using tetrahydrofuran is more efficient than that using methanol. This could be due to the possible interaction and dilution of the reagents in the solvent. It is clear that the catalytic conversion of catechol to o-quinone is influenced by the properties of the solvent [42], particularly its dielectric constant, the dipole moment, and the polarity of the complexes.

- Effect of ligand concentration on the catecholase activity

To study the effect of ligand concentration on the catecholase activities, the concentration of the metal salt was decreased to be one equivalent for two equivalents of ligand to form the catalyst; the summary of the ligand/salt ratio effects on the reaction rates is shown in Table 3. As shown, the effect of the concentration of the ligand allows a considerable increase in the reaction rate. The oxidation rate of the complex L1/$CuSO_4$ was increased from 4.86 to 9.31 µmol L^{-1} min^{-1}, whereas that of complex L3/$CuCl_2$ was augmented to 25.1 µmol L^{-1} min^{-1}. These results can be explained essentially by the increase in the concentration of complexes formed in situ. Figure 1

In the case of (1L/2M) ratio, the excess of metal salt concentration leads in several cases to decrease the oxidation rates. The high catalytic activity reaches 11.54 µmol L^{-1} min^{-1} when (L2/Cu$(CH_3COO)_2$) ratio is used while the low activity 0.97 µmol L^{-1} min^{-1} when (L1/Cu$(NO_3)_2$) is used (Table 3).

- Kinetic study

To understand more the extent of the catalytic efficiency of the complexes prepared in situ, kinetic studies determined by the initial rate method were performed. The experiments were carried out in methanol, maintaining the concentration of L1/Cu$(NO_3)_2$ and L2/$CuSO_4$ catalyst in situ at a specific value of 2×10^{-3} mol L^{-1} and the variation of the concentration of the 1,2-dihydroxybenzene (catechol) substrate from 1×10^{-3} to 2×10^{-1} mol L^{-1}. The evolu-

Table 4
Values of the V_{max} and K_m of the reaction catalyzed by various types of ligands and metal salts.

Combination of Li/Salt	V_{max} (µmol L^{-1} min^{-1})	K_m (mol L^{-1})
L1/Cu$(NO_3)_2$	1.53	0.001
L2/$CuSO_4$	5.26	0.045

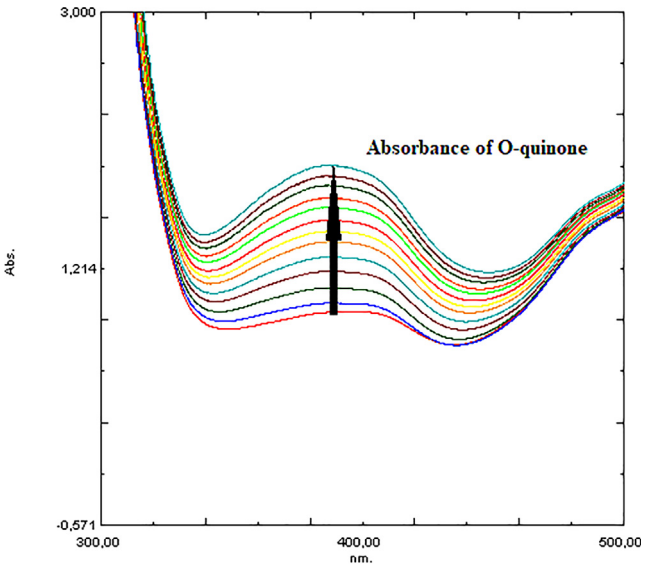

Fig. 8. Absorbance spectrum of o-quinone as a function of time for the combination L1/Cu$(NO_3)_2$ in methanol.

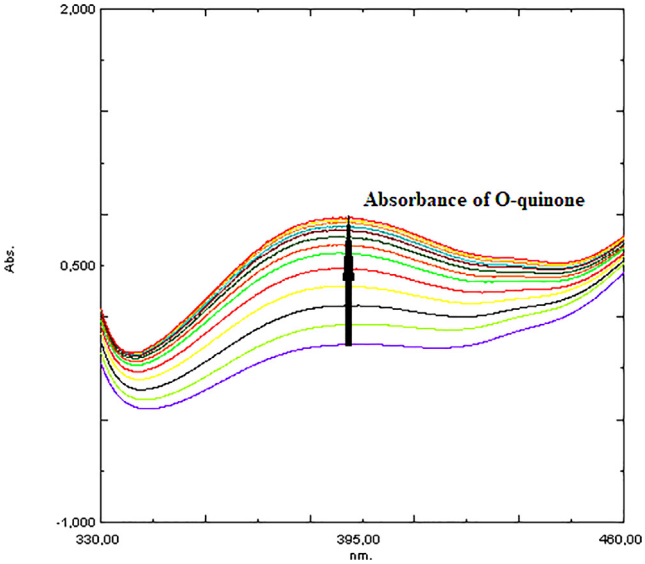

Fig. 9. Absorbance spectrum of o-quinone as a function of time for the combination L1/Cu$(CH_3COO)_2$ in THF.

tion of absorbance of o-quinone at 390 nm was monitored for the first 5 min of the reaction time, the linear relationship between the initial rates and the substrate concentration was obtained. The Michaelis-Menten model is applied to obtain the kinetic parameters of the best catalyst. Fig. 7 shows the Michaelis–Menten model for some best complexes formed in situ. The value K_m and V_{max} for the two catalysts are presented in Table 4. The results showed that the rates vary between 1.53 and 5.26 μmol L^{-1} min^{-1}, and the constants K_m are between 0.001 and 0.045 mol L^{-1}. The best catalytic process was obtained when using L2/$CuSO_4$ in methanol solvent.

- UV–Vis spectrophotometric study

The oxidation of catechol was evaluated by monitoring the increase in the intensity of o-quinone at λ_{max} 390 nm after mixing of 0.15 mL of ligands, 0.15 mL of copper salts, and 2 mL of catechol. The o-quinone absorbance was recorded at a time interval of every 5 min. Figs. 8 and 9 shows the absorbance spectrum of o-quinone as a function of time when the process involved the use of combination L1/$Cu(NO_3)_2$ in methanol and L1/$Cu(CH_3COO)_2$ in tetrahydrofuran.

4. Conclusion

In summary, five ligands containing naphthalene and benzene moieties ponded by aza group are reported and studied for their catecholase activity with different copper salts (II). These ligands can provide N,O-bidentate chelation to stabilize transition or main group metal complexes. Excellent catalytic activity was obtained. The catalytic activities of the complexes formed in situ, and several metallic salts were found to be influenced by the nature of the ligand, the anion in the metal salt, the solvent and the ratios of ligands and metal salts. This study proved that the current ligands can be used as a model for further development in the process of catecholase activity.

CRediT authorship contribution statement

Nadia Bouroumane: Conceptualization, Methodology, Investigation, Writing - review & editing. **Mohamed El Boutaybi:** Resources, Investigation. **Souheyla Chetioui:** Resources, Investigation. **Hassiba Bougueria:** Resources, Investigation. **Amel Djedouani:** Supervision, Validation, Writing - review & editing. **Zahra Bahari:** Supervision, Validation, Writing - review & editing. **Adyl Oussaid:** Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matpr.2021.03.076.

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